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By: G. F. D'Alelio, Principal Investigator

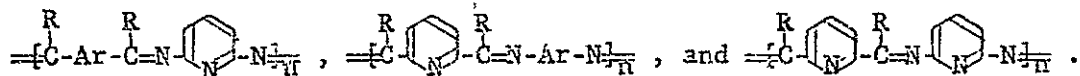
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EXPLORATORY POLYMER SYNTHESIS

- I. Reprints of the following papers based on research supported in part under this grant and in part under NASA Grant 15-004-038 (sponsored by NASA-Ames Laboratory, Moffett Field, California) were received and the required copies forwarded to Office of University Affairs, Code Y, NASA, Washington, D. C.
- A. D'Alelio, G.F. and R.K. Schoenig, Polymeric Schiff Bases. XII. The Syntheses and Thermal Stabilities of Polyazines and Derived Polystilbenes. J. Macromol. Sci.-Chem., A2(5), pp. 979-1043 (1968).
- B. D'Alelio, G.F., D.M. Feigl, H.E. Kieffer, and R.K. Mehta, Polymeric Schiff Bases. XIII. The Direct Synthesis of Cross-Linked Polymeric Azomethines. J. Macromol. Sci.-Chem., A2(6), pp. 1223-1234 (1968).
- C. D'Alelio, G.F., R.K. Mehta, D.M. Feigl, H.E. Mieffer, and R.L. Germonprez, Polymeric Schiff Bases. XIV. The Synthesis of Cross-Linked Polymeric Azomethines by Exchange Reactions. J. Macromol. Sci.-Chem., A2(6), pp. 1235-1259 (1968).
- D. D'Alelio, G.F., H.E. Kieffer, R.L. Germonprez, and R.K. Mehta, Polymeric Schiff Bases. XV. The Synthesis of Cross-Linked Polymeric Azomethines from Amino Aryl Ketones. J. Macromol. Sci.-Chem., A2(6), pp. 1261-1269 (1968).
- E. D'Alelio, G.F., F.R. Meyers, W.F. Strazik, and R.L. Germonprez, Polymeric Schiff Bases. XVI. Alternative Syntheses for the Imino-benzylidene Polymers. J. Macromol. Sci.-Chem., A2(7), pp. 1333-1351 (1968).
- F. D'Alelio, G.F., W.F. Strazik, D.M. Feigl, and R.K. Schoenig, Polymeric Schiff Bases. XVII. Azomethine Copolymers. J. Macromol. Sci.-Chem., A2(8), pp. 1457-1492 (1968).
- II. No further effort has been expended on Schiff base polymers containing o-hydroxy substitution (cf. Report No. 16, Item III, p. 3, NASA Grant NsG339).
- III. The entire research effort is being directed to the synthesis of polymers of enhanced conductivity and to the exploration of the structural parameters which contribute to conductivity. As the first approach to

achieving this objective, polymeric azomethines which contain heterocyclic aromatic tertiary nitrogen atoms as part of the linear chain have been selected as candidates. These polymer systems were described in the research proposal for this grant submitted to NASA October 1, 1968. Typical polymers are the polyazomethines related to the Schiff bases in which the benzene rings are replaced by pyridine rings, e.g.,

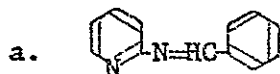


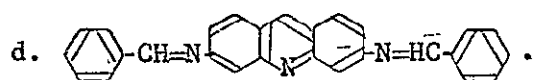
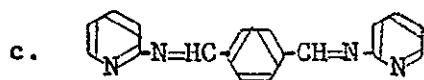
These polymers can (1) be used as donors in charge-transfer complexes, (2) quaternarized permitting the attachment of short or long branches (including dipole dye molecules) to the backbone, and (3) the quaternarized ionic site can be complexed with acceptors to yield charge transfer complexes.

Since it is important that the parameters that contribute to conduction be understood, and since polymer molecules themselves are complex substances in which the causes for small or subtle changes in properties are difficult to establish, it was considered essential that prototype monomeric molecules, which are similar in structure to the repeating units in the polymer molecules, be studied first and understood. For this reason the research has been divided into two parts. The first part deals with monomers, their syntheses and their prototype reactions; the second part deals with the polymers.

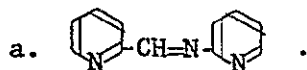
IV. Monomers.

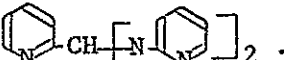
1. The following monomers of high purity have been synthesized and characterized by elemental analyses, infrared spectra, melting points and solubility.





2. The syntheses of the following monomers were also attempted:

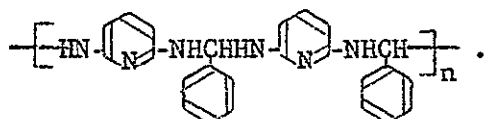


The elemental analysis of the isolated product was poor, and its infrared spectrum indicated high contamination with the bis-compound, .

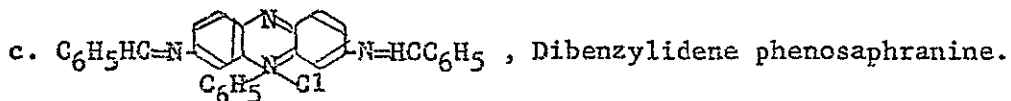
This synthesis will be attempted again under different experimental conditions.



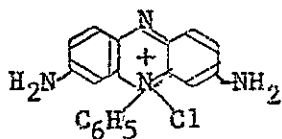
The elemental analysis of the isolated product was not satisfactory. Its infrared spectrum indicated a polymeric nature and showed strong bands for -NH. Its molecular weight, determined by vapor phase osmometry, was 1200. The data indicate that the repeating structural units are:



This synthesis has been repeated under different experimental conditions, the product has been fractionated and the fractions are being characterized.

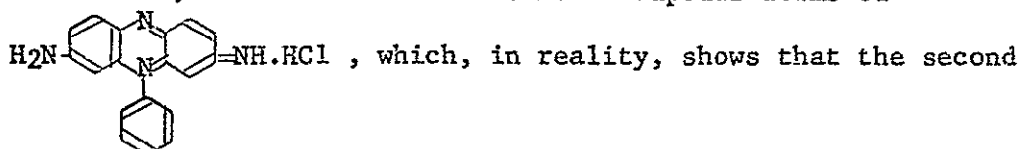


Numerous efforts were made to prepare this model quaternarized bis-Schiff base from benzaldehyde and phenosaphranine,

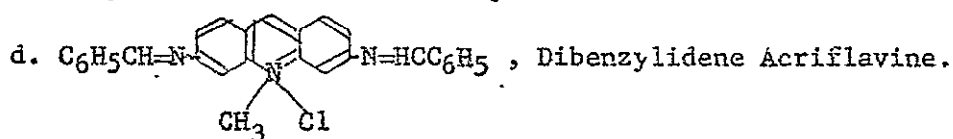


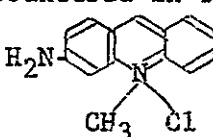
In spite of our broad experience in Schiff base syntheses, none of

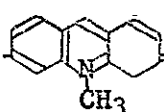
these experiments was successful. The elemental analyses and the infrared spectra were unsatisfactory; the data obtained indicated that the derivatives were mono-Schiff bases. These results were most puzzling since the second amino group could not be made to react with benzaldehyde to give a di-Schiff base. A literature study on the syntheses of phenosafranine showed that the formula as written, is for one of the isomeric dipolar forms of

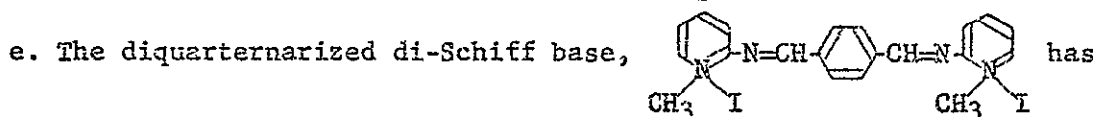


amino group is a ketamine, and not a true amino compound, which could not react with aldehydes to yield a Schiff base. Therefore, only a mono-Schiff base is possible.

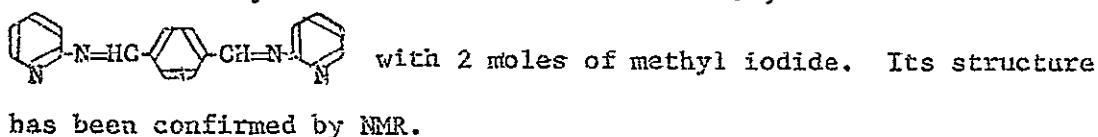


The experiences encountered in the attempts to react benzaldehyde with acriflavine, H_2N  $=\text{NH}_2$, paralleled those of pheno-

safranine. Only the mono-Schiff base could be obtained because the formula usually written for acriflavine is an isomeric form of the ketamine and thus only a mono-Schiff base, the mono-benzylidene acriflavine, $\text{C}_6\text{H}_5\text{CH}=\text{N}$  $=\text{NH} \cdot \text{HCl}$, can be obtained.



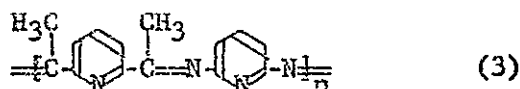
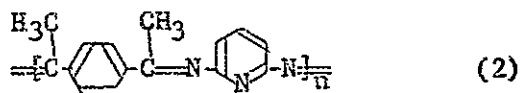
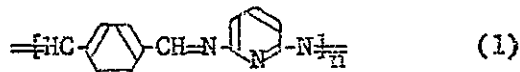
been obtained by reaction of the di-Schiff base,



The same compound was obtained when the di-Schiff base was reacted with 4 moles of methyl iodide, establishing the important fact that the $-\text{CH}=\text{N}-$ Schiff base moiety was not methiodated but that only the pyridine nitrogen was quaternarized. This would indicate that the polymers can be quaternarized at the pyridine nitrogen without reaction at the Schiff base linkage; reaction at the Schiff base moiety, $-\text{C}=\text{N}-$, would destroy the conjugation of the linear chain and potential conductivity.

V. Polymers.

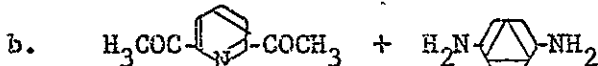
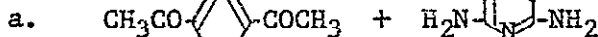
1. All the polymer studies performed to date have been of a preliminary and exploratory nature, to establish the parameters for satisfactory synthesis. This work was initiated to accelerate the project while developing unequivocal data on the prototype reactions of the monomers.
2. A number of polymeric azomethines containing pyridine rings in the backbone have been prepared by condensing 2,6-diaminopyridine with (1) terephthalaldehyde, $p\text{-OHCC}_6\text{H}_4\text{CHO}$; (2) 1,4-diacetyl benzene, $p\text{-CH}_3\text{COC}_6\text{H}_4\text{COCH}_3$ and (3) 2,6-diacetyl pyridine, $\text{H}_3\text{COC}-\text{C}_5\text{H}_3\text{N}-\text{COCH}_3$, respectively, to polymers presumed to have the following structures respectively,



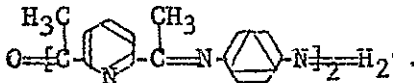
and (4) by the reaction of *p*-phenylenediamine with 2,6-diacetyl pyridine to a polymer of the probably structure,



Studies will be continued to establish the experimental parameters required to give high molecular weight polymers with good solubility in appropriate solvents. Studies will be continued on the following selected systems which show promise:

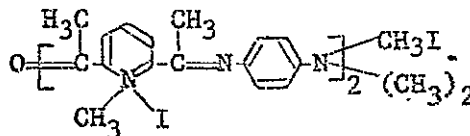


quaternarization post-reactions. The elemental analysis and infrared spectroscopy indicated that its structure was



A sample of the oligomer was cast from DMAC solution and it showed fair film forming properties. When TCNE was added to the solution, in a ratio of 1 mole TCNE per each mole of pyridine nitrogen, a considerable darkening of the solution occurred. The films cast from this solution were better than from the original oligomer; and the elemental analysis indicated a 1:1 complex of TCNE per mole of pyridine ring.

It was subjected to quaternarization with an excess of CH_3I ; the elemental analysis of the reaction product and its infrared spectrum indicated that quaternarization did indeed take place on the pyridine nitrogen and, as expected, alkylation of the terminal $-\text{NH}_2$ group also took place. The probable structure of the product is:



The product showed some solubility in water.